



ent By: D.J. LOCKWOOD IMS;

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Dec-23-03 13:06;

Page 2

**PATENT****IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re Application of

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Art Unit: 1641

Boukherroub, Rabah

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)Examiner: CEPERLEY, MARY

Serial No: 09/803,044

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Filed: March 12, 2001

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Agent's Docket no. 10963-US

December 23, 2003

For: PASSIVATION OF POROUS SEMICONDUCTORS

Honorable Commissioner of Patent and Trademarks

Alexandria, Virginia 22313-1450

**DECLARATION UNDER 37 CFR 1.132**

I, David Lockwood, of 99 Ida Rochelau Place, Vanier, Ontario, K1L 8L6 do hereby declare that:

1. I am one of the named inventors in the above-reference application and as such have knowledge of the facts herein set forth. I am currently a principal research officer at the National Research Council in Ottawa. I hold a PhD and Doctor of Science in solid state physics. I have written over 450 scientific publications in the field of optical properties of solids. I am a Fellow Royal Society of Canada and the American Physical Society.

2. The invention relates to porous silicon (PSi), which is a distinct and identifiable material recognizable to persons skilled in the art as different from ordinary bulk silicon having unique properties. For example, one skilled in the art would not consider a silicon crystal that contained a few shallow pores in the surface as being "porous silicon" as the

USSN 09/803,044

Art Unit 1641

expression is currently understood by one skilled in the art since the properties of such material would not be significantly changed.

3. Ordinary bulk silicon forms a diamond-structured crystal lattice that has been used as a material in semiconductor applications for many years. The surface can be polished smooth.
4. PSi has a porous layer consisting of a complicated network of silicon wires, each with a thickness of between 2-5 nm lying on a wafer of bulk silicon. The pores typically extend about 30 microns into the surface of the bulk silicon wafer. The porous layer loses its normal crystalline structure in the process.
5. The porosity of PSi is defined as the amount of air in the material after processing has finished, so a 45% porous sample would contain 45% air and 55% silicon. A typical sample could have an internal surface area of up to several hundred square meters per cubic centimeter.
6. The presence of the pores changes the physical nature of the material such that PSi has properties not exhibited by bulk silicon. For example, PSi emits light mainly in the visible region of the electromagnetic spectrum. The emission has the unique property that the wavelength of the emitted light can be changed simply by increasing or decreasing the porosity of the material. A highly porous sample (70-80% porosity) will emit green/blue light while a less porous sample (40%) will emit red light.
7. PSi is made by dissolving a bulk silicon wafer in an electrochemical cell containing hydrogen fluoride solution using anodic etching. See, for example, US patent no. 5,965,005.
8. In order to qualify as PSi, as the term would be understood in the art, the material has to have sufficient porosity to materially change the properties of the material at the electronic level. Attached hereto as exhibit A is a copy of a paper published in the American Physical Society journal entitled "Electrical band-gap energy of porous silicon and the band offsets at the porous-silicon/crystalline-silicon heterojunction measured versus sample temperature", J. T. Frederiksen, P. G. Melcher, and E. Veje, 1998. It is clear from this paper that crystalline silicon (c-Si) and porous silicon (PSi) represent distinct and readily identifiable materials.

USSN 09/803,044

Art Unit 1641

9. Ordinary crystalline silicon (c-Si) will form an oxidation layer on its surface when exposed to air. Consequently, in order to process the c-Si, this oxidation layer must first be removed. This removal is typically carried out using an HF (hydrofluoric acid) etching solution. Treatment in HF produces a smooth surface and does not ordinarily produce PSi unless the etching takes place through a mask.

10. I have read the Sieval paper cited by the Examiner. Nowhere in this paper is porous silicon mentioned, and upon a review of the paper it is quite clear to me that the paper relates to crystalline silicon, not porous silicon. In the passage referred to by the Examiner on page 1761 relating to the monolayer preparation, the "piece of silicon" is treated in 2% hydrofluoric acid. This treatment is conventional on crystalline silicon and does not create PSi as the term is understood in the art. The treatment is necessary to remove the native oxide layer and to replace the oxygen atoms by a hydrogen-terminated silicon surface so that the alkenes can react with the hydrogen-terminated surface (see Figure 1 of Sieval). The first paragraph in the right hand column confirms this by referring to the "freshly etched and cleaned silicon background crystal instead of the oxidized surface".

11. I disagree with the Examiner's statement on page 3 of the office action that the "solid silicon of Sieval is made "porous" by the same method as that used in the instant invention". The mere etching with HF to reduce the oxidation layer as taught by Sieval does not produce PSi in the absence of anodic treatment. The method is not the same as that taught in the present application since the specification teaches that the HF treatment took place in the presence of an exemplary current density of  $5\text{mA}/\text{cm}^2$ . See, page 7, line 19 of the specification. The fabrication of porous silicon per se in an electrochemical cell is well known and does not form part of the invention.

12. The problem solved by the invention is that the photoluminescence of conventional PSi is subject to gradual degradation due to photoluminescence quenching caused by the presence of chemical adsorbates. My co-inventors and I discovered that this problem can overcome by treating the porous structure in the presence of an alkene reactant in the manner defined in claim 1. The fact that porous silicon treated with alkenes in this manner resulted in structures that are highly stable against

USSN 09/803,044

Art Unit 1641

photoluminescence degradation was unexpected, and this result is nowhere reported in the prior art.

13. The Sieval paper, which is of a highly theoretical nature, says little about the purpose of the monolayers. Exemplary applications disclosed in Sieval are "nonlinear optics" and "adsorption experiments". In the case of "adsorption experiments", for example, one would wish to treat the silicon surface with a material capable of attracting the species to be adsorbed. The objective would be to produce a monolayer that was stable, that is it did not easily become detached from the surface.

14. It should be noted that the word "stable" is used in an entirely different context in Sieval from the present application. The starting point in Sieval is that there is a need to provide a monolayer on the surface of a silicon crystal for some purpose, which is not well explained in Sieval, although one example suggested is that the monolayer is provided for purposes of adsorption (see above). The problem faced by Sieval is that such a monolayer is likely to be thermally unstable in the sense it is likely to become easily detached from the silicon crystal at high temperature. Sieval teaches that his particular monolayers have remarkably high thermal stability (see, for example, the abstract). By this he clearly means that his monolayers do not become detached easily as the temperature rises. This property has nothing to do with the stability sought by the present inventors, which is the ability of the porous silicon, not the monolayer, to retain its photoluminescence properties over a long period of time.

15. Sieval relates to crystalline silicon with a surface that is smooth or nearly smooth at the atomic level. While Sieval mentions surface "roughness" in his paper, it is clear that he is only referring to roughness at the atomic level. The roughness given in his table 2 is in the order of 1 to 4 Å due to the surface layer of SiH, SiH<sub>2</sub> and SiH<sub>3</sub> groups. At the microscopic level this would be considered an extremely smooth surface.

16. In his "Conclusions" on page 1768, Sieval refers to the silicon (100) surface. Porous silicon no longer has a (100) surface due to the nature of the pores.

17. Porous silicon (PSi) with its multitude of pores extending up to 30 microns into the silicon surface has a roughness that goes way beyond the atomic scale envisaged by Sieval. In view of the fact that Sieval's teachings clearly relate to crystalline silicon with

ent By: D.J. LOCKWOOD IMS;

613 993 6486;

Dec-23-03 13:07;

Page 6

USSN 09/803,044

Art Unit 1641


a surface that is smooth at the microscopic level, and although he considers it worthy of mention that his teachings still apply to a surface that is not flat at the atomic level, it is unreasonable to suppose that one skilled in the art would consider Sieval's teachings applicable to PSi, where the deliberately introduced porosity goes way beyond the atomic scale in roughness.

18. Sieval teaches that in order to achieve the results specified, a dense and ordered monolayer is desired (see first paragraph of Conclusions on page 1768). Such dense and ordered monolayers would not be achievable with porous silicon due the macroscopic roughness of its surface (In the case of porous silicon, one can actually see the surface roughness with an unaided eye). Such roughness would clearly not permit the formation of the monolayers desired in Sieval.

19. I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signed

  
David J LockwoodDate: December 23, 2003

CERTIFICATE OF TRANSMISSION BY FACSIMILE (37 CFR 1.8)			Docket No. 10963-US
Applicant(s): Rabah BOUKHERROUB, et al.			
Serial No. 09/803,044	Filing Date March 12, 2002	Examiner CEPERLEY, Mary	Group Art Unit 1641
Invention:  PASSIVATION OF POROUS SEMICONDUCTORS			
<p>I hereby certify that this <u>Declaration under 37 CFR 1.132</u> <small>(Identify type of correspondence)</small></p> <p>is being facsimile transmitted to the United States Patent and Trademarks Office (Fax. No. <u>703-872-9306</u>)</p> <p>on <u>December 31, 2003</u> <small>(Date)</small></p> <p style="text-align: right;"><u>Richard J. Mitchell 34519</u> <small>(Typed or Printed Name of Person Signing Certificate)</small></p> <p style="text-align: right;"> <small>(Signature)</small></p> <p style="text-align: center;">Note: Each paper must have its own certification of mailing.</p>			

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